Magnetic excitations in multiferroic $TbMnO_3$

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The magnetic excitations in multiferroic $TbMnO_3$ have been studied by inelastic neutron scattering in the spiral and sinusoidally ordered phases. At the incommensurate magnetic zone center of the spiral phase, we find three low-lying magnons whose character has been fully determined using neutron-polarization analysis. The excitation at the lowest energy is the sliding mode of the spiral, and two modes at 1.1 and 2.5 meV correspond to rotations of the spiral rotation plane. These latter modes are expected to couple to the electric polarization. The 2.5 meV-mode is in perfect agreement with recent infra-red-spectroscopy data giving strong support to its interpretation as an hybridized phonon-magnon excitation.

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The perovskite $TbMnO_3$ [1] is a key material for the new class of multiferroic transition metal oxides [2, 3, 4], since the polarization in the ferroelectric phase is sizeable and since the magnetoelectric coupling is remarkably large [1, 5]. The antiferro-type ordering of the single-occupied e_g-orbitals implies a ferromagnetic nearest neighbor (nn) interaction J_{FM} in $LaMnO_3$ as well as in $TbMnO_3$ [6], but in $TbMnO_3$, a large c-axis octahedron rotation [7] yields a sizeable overlap of the e_g-orbitals of next-nearest neighbor sites (nnn) along b rendering the associated magnetic interaction strongly antiferromagnetic, J_{nnn} [6]. The well-defined ferromagnetic order in the a, b planes of $LaMnO_3$, therefore, becomes strongly frustrated in $TbMnO_3$ giving rise to the complex magnetic ordering which finally causes the multiferroic behavior.

At T_N=42 K, the Mn spins in $TbMnO_3$ order in a longitudinal spin-density wave (SDW) with a wave-vector of $\mathbf{q}$=(0,0.28,0) in reduced lattice units of the *Pbnm*-structure [8, 9]. Upon further cooling, the modulation vector changes slightly until at T_C=28 K a second transition into a spiral phase occurs [1, 9]. Here, the magnetic order corresponds to an elliptic cycloid still modulated along the b-direction but with the spins rotating around the a-axis [9]. Associated with this SDW to spiral transition, the spontaneous electric polarization parallel to the c-axis appears.

The appearance of the electric polarization at the transition into the spiral phase was microscopically explained by Katsura et al. [10]. This idea was followed by studies of the phenomenology [11] and its extension to the lattice interaction [12]. Due to the non-collinear spin arrangement in the spiral phase, the inverse of the Dzyaloshinski-Moriya interaction implies an uniform displacement with an electric polarization given by:

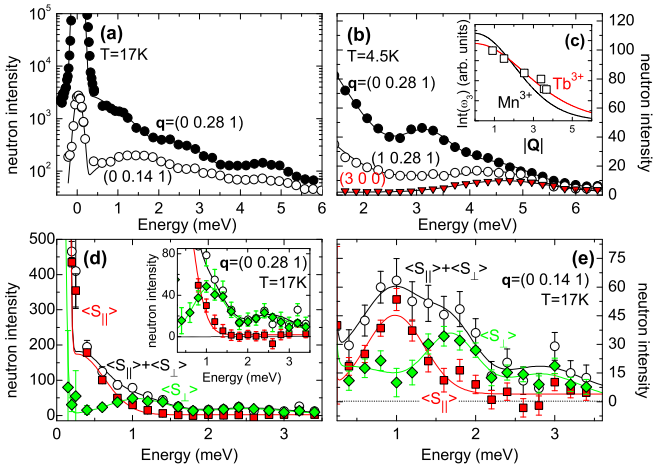

FIG. 1: (color online) Raw-data scans at the incommensurate zone center and at the b-axis zone boundary in the spiral phase (PANDA and 4F, k_f=1.5Å^{-1}) a); **Q**-dependence of the signal b), the insert c) compares the suppression of the 4.5 meV feature with the expectation due to a Tb magnetic form factor (PUMA, k_i=2.66Å^{-1}). Full polarization analysis of the magnetic excitations at the incommensurate zone center and at the zone boundary (IN14, k_f=1.5Å^{-1}) d) and e).

$$\mathbf{P} \propto \mathbf{r_{ij}} \times (\mathbf{S_i} \times \mathbf{S_j}) \quad (1),$$

for a pair of spins $\mathbf{S_i}$,$\mathbf{S_j}$ with a distance vector $\mathbf{r_{ij}}$. Considering the mechanism in equation (1) there is a close coupling between the dielectric properties and the magnetic excitations which should lead to hybridized phonon-magnon excitations. First evidence for such mixed excitations was recently obtained in Infra-Red (IR) optical-spectroscopy measurements [13],however, their role in the multiferroic behavior is unclear as their magnetic coun-

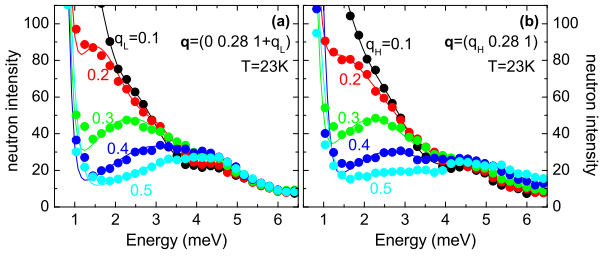

FIG. 2: Raw-data scans to determine the magnon dispersion in $TbMnO_3$ along a and c directions starting at the incommensurate zone center (0,0.28,1), (PUMA, k_i=2.662Å^{-1}).

terparts have been little explored thus far [14].

In this letter we present the results of inelastic neutron scattering (INS) experiments to unravel the magnetic excitations in $TbMnO_3$, in particular the low-energy modes relevant for the multiferroic behavior whose characters were determined using longitudinal polarization analysis. The excellent agreement with the IR studies strengthens the evidence for mixed excitations.

A ∼900 mm^3 large untwinned single crystal of $TbMnO_3$ was grown using an image furnace [15]. The crystal exhibits the magnetic transitions at 42 and 28 K in agreement with previous studies [1, 9]. INS experiments were performed on various triple-axis spectrometers : on 4F (cold neutrons, Laboratoire Léon Brillouin), on PANDA (cold neutrons) and PUMA (thermal beam, both at the Forschungsreaktor München II) and using full polarization analysis with the CRYOPAD setup on IN14 (cold neutrons, Institut Laue Langevin). Measurements were taken in the ferroelectric (T=17 and 23 K), in the paraelectric SDW and in the paramagnetic phases.

Fig. 1 shows scans taken at the incommensurate zone center $\mathbf{Q}$=(0,0.28,1) and at the zone boundary in b direction in the spiral phase at T=17 K. Typical scans to determine the dispersion along the a and c-directions are shown in Fig. 2; along these directions the frequencies rapidly increase. In all scans we find an excitation at 4.5 meV which in agreement with the interpretation in reference [14] can be identified as a Tb crystal-field excitation, since it does not disperse and since it exhibits a weaker dependence on the length of the scattering vector, $|\mathbf{Q}|$, compared to the other contributions. The $|\mathbf{Q}|$-dependence, furthermore, is in good agreement with the Tb magnetic form factor, see Fig. 1 c).

Fig. 3 shows the magnon dispersion of $TbMnO_3$ obtained in the spiral (T=23 and 17 K) and in the paraelectric SDW phase (T=32 K). The dotted lines in Fig. 3 denote the magnon dispersion measured in $LaMnO_3$ [16]. Only along the antiferromagnetic c-direction, $LaMnO_3$ and $TbMnO_3$ exhibit a qualitatively similar dispersion. Along the a, b plane, the dispersion is essentially flattened in $TbMnO_3$. The upper cut-off energy in $TbMnO_3$ amounts to ∼8 meV, whereas magnon energies in $LaMnO_3$ extend up to 33 meV [16]. The pronounced softening of the magnon frequencies for wave vectors along the ferromagnetic planes reflects the frustrating nnn interactions and the weakened nearest neighbor interaction [6]. The magnons in $TbMnO_3$ are broadened, and we find evidence for a splitting of excitations even in the SDW phase, which, however, requires further studies. Tentatively, we may describe the dispersion along a and c in a S=2 Heisenberg model with a single magnon branch including single-ion anisotropy, D. Thereby, we obtain the interaction parameters J_{FM}=0.15(1)meV (nearest neighbors along the a, b planes) and J_{AFM}=-0.31(2)meV (neighbors along c) and D=0.09(1)meV. These values should be compared to the values of J_{FM}=0.83 meV and J_{AFM}=-0.58 meV observed in $LaMnO_3$ [16] . In the spiral phase, mode splitting is observed throughout the Brillouin zone and a more sophisticated model to fully describe the spin-excitation dispersion is needed.

Concerning the high-energy part of the dispersion, our data agree qualitatively with the study of the magnon dispersion by Kajimoto et al. [14], but the splitting in the excitations has not been analyzed in reference [14] probably due to the fact that this group did not analyze the dispersion starting at the incommensurate zone center. In addition, we have explored in detail the low-energy part of the dispersion at the incommensurate zone center and the soft branches along the b-direction. As seen in Fig. 1 and in the dispersion along the b direction shown in Fig. 3 a), there are actually three low-energy branches emerging out of $\mathbf{Q}$=(0,0.28,1) . In view of the magnetoelectric effect, these are the most relevant modes. The unpolarized data in Fig. 1 a) show the three contributions (plus the Tb crystal field at 4.5 meV), but this type of data does not allow us to determine unambiguously the polarization of the different contributions in spite of the many different Brillouin zones explored.

We have employed longitudinal polarization analysis yielding important additional information : in the spin-flip scattering channel only those excitations are detected whose polarization is perpendicular to the chosen neutron-polarization axis [17]. We have performed the experiment with the a direction vertical to the scattering plane using the CRYOPAD-device on IN14. The setup yielded a remarkable precision with a flipping ratio of $I^{NSF} : I^{SF} = 35$ and an accuracy of about 2% in the transverse polarization terms. With the three neutron-polarization directions : parallel to $\mathbf{Q}$, (x), parallel to a, (z), and perpendicular to both $\mathbf{Q}$ and a, (y), one may distinguish between excitations polarized perpendicular to the spiral plane in $TbMnO_3$ (i.e. perpendicular to the b, c spiral plane, $S_\perp$) and those polarized within the spiral plane (i.e. in the b, c plane, $S_\parallel$). In the spin-flip (x)-channel the sum of both magnetic contributions appear, whereas the spin-flip (y) and (z) channels measure only the $S_\perp$ and the $S_\parallel$ contribution, respectively [17]. By subtracting the intensities obtained in different channels one directly obtains $S_\perp$ and $S_\parallel$ without any background assumption. The two contributions $S_\perp$ and $S_\parallel$ are separated in the lower part of Fig. 1. At the incommensu-

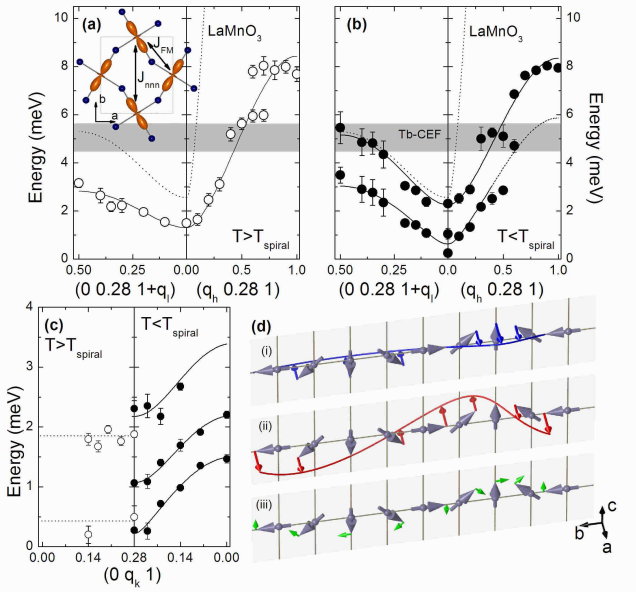

FIG. 3: Dispersion of the spin-wave excitations in $TbMnO_3$ along the a and the c directions of the $Pbnm$ lattice in the paraelectric sinusoidal phase a) and in the ferroelectric spiral phase b) . Dispersion along the modulation vector in the spiral and in the SDW phase c). Polarization of the three low-energy modes at the incommensurate zone center d) : the two a-polarized modes, (i) and (ii), and the sliding mode of the spiral, (iii), see text.

rate zone center, the excitation with the lowest energy of 0.2(1) meV is b, c polarized. Since one may exclude a longitudinal spin excitation in this high-moment ordered structure, this mode must be attributed to the transverse magnon polarized in the spiral plane. This mode is the sliding mode of the modulated magnetic structure its polarization scheme is shown in Fig 3d)(iii). It has no impact on equation (1) describing the magnetoelectric coupling. Therefore, it should not be relevant for the multiferroic behavior. Since the spiral in $TbMnO_3$ is not perfectly circular an anisotropy term can explain a finite energy of the sliding mode in addition to pinning effects.

In the $S_\perp$ channel, there are two contributions at energies of 1.08(8) and 2.46(9) meV. The low-energy excitation of a multiferroic system where ferroelectricity originates from the inverse Dzyaloshinski Moriya interaction has been discussed recently by Katsura et al. [18]. Besides the sliding mode and the phonons, there are indeed two magnetic excitations with a spin polarization perpendicular to the spiral plane (b, c plane in the case of $TbMnO_3$) corresponding to $S_\perp$. These modes are illustrated in Fig. 3d) i) and ii). For simplicity, we assume that the phase shift between the b and the c components of the spiral in $TbMnO_3$ is exactly $\pi/2$ and that the two coefficients are of equal size, i.e. the spiral is circular. Then, one may describe the magnetic order by :

$$\mathbf{S_i} = S \cdot \cos(\mathbf{q_{spiral}} \cdot \mathbf{R_i}) \cdot \mathbf{e_y} + S \cdot \sin(\mathbf{q_{spiral}} \cdot \mathbf{R_i}) \cdot \mathbf{e_z} \quad (2),$$

where $\mathbf{R_i}$ is the position vector of the spin $\mathbf{S_i}$. An a-polarized magnetic excitation at the incommensurate zone center necessarily possesses the same modulation along b, however the oscillating part can be in-phase either with the b component (cosine term in equation (2), see Fig. 3d) (ii)) or with the c component (sine term in equation (2), see Fig. 3d) (i)). The arising polarization patterns are distinct : in the first case the spiral plane rotates around the c direction and it rotates around b in the second case. Correspondingly, the cross product $\mathbf{S_i} \times \mathbf{S_j}$ between neighboring spins rotates around the c direction and around the b direction in these cases. Since the modulation vector or $\mathbf{r_{ij}}$ in equation (1) remain always parallel b, the rotation of the $\mathbf{S_i} \times \mathbf{S_j}$ cross product through the magnon has a strong linear coupling to the polarization in the second case, which we label ω_- following reference [18]. The ω_--excitation is the Goldstone boson of the multiferroic phase, it may shift to finite energy due to anisotropy terms. It is a magnon-phonon hybridization with the phonon describing the electronic polarization along the a direction. The other transverse magnon couples only quadratically, and thus weakly, to the polarization. It weakly modulates the static polarization parallel to c. Both magnons posses finite frequencies due to anisotropy effects.

Recently, Pimenov et al. [13] have reported the observation of a low-energy excitation in IR spectroscopy studies of $GdMnO_3$ and $TbMnO_3$ which could be fully suppressed by applying an external magnetic field. They interpreted this excitation as an electromagnon, the hybridized magnetic and phononic excitation. This result together with the analysis given in reference [18] agree perfectly with our INS study of the magnetic excitations. The electromagnon feature seen by Pimenov et al. at $20cm^{-1}$=2.48 meV agrees with one of the low-lying magnetic excitations in the $S_\perp$ contribution. We, therefore, tentatively attribute the 2.46 meV neutron-scattering excitation to the ω_- Goldstone boson. According to the analysis given above, this mode should couple to the polarization in the a-direction, which is indeed the direction of electric field in the IR experiment sensing the lattice part of the excitation. In $TbMnO_3$ the spiral order might be more complex than the ideal circular cycloid considered in equation (2); therefore the characters of the two $S_\perp$-polarized magnetic excitations might weakly mix rendering both IR-active. It is interesting to note that also the energy of the lower $S_\perp$ mode agrees perfectly with the - though weaker - feature in the IR response at 1.24 meV in reference [13]. We emphasize, that associating the 2.46 meV neutron-scattering excitation with the ω_--mode only bases on the comparison with the IR results; actually one might expect this mode to exhibit a lower energy since it describes the flip of the spiral into the a, b-plane which seems to occur in $TbMnO_3$ under field as well as in related $ReMnO_3$ [2, 6, 15].

Along the b direction the three low-energy branches can be followed till the incommensurate zone boundary and even beyond in the spiral phase. The disper-

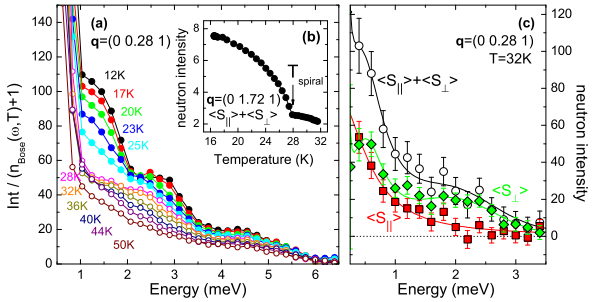

FIG. 4: (color online) Temperature dependence of the magnetic scattering at the incommensurate zone center determined with unpolarized neutrons (PUMA, k_i=2.662 Å^{-1} constant) a) and with polarized neutrons (IN14, k_f=1.5 Å^{-1} constant) c); the inset b) shows the magnetic elastic scattering at **Q**=(0,1.72,1) as function of temperature.

sion unambiguously shows that anisotropy terms play a dominant role in $TbMnO_3$; they appear to determine the sequence of magnetic phases as function of temperature and magnetic field. Introducing the frustrating J_{nnn} interaction into the non-frustrated magnon dispersion along b, see insert in Fig. 3a), one may understand the b-dispersion in the incommensurate phase. The frustration generates a dispersion minimum whose position as well as the analysis of the exchange energy in the ordered state allow one to estimate the interaction ratio to be of the order of $J_{nnn}/\ J_{FM}$=0.8. The finite energies of both the ω_- feature and the other a-polarized zone-center magnetic excitation arise from either a single-ion anisotropy, from exchange anisotropy or from the electron-lattice coupling. More experimental and theoretical efforts are, however, needed in order to fully characterize the aspects arising from folding the magnon dispersion into the incommensurate ordering.

The inset of Fig. 4 shows the spin-flip signal at the (0,1.72,1) magnetic Bragg reflection which essentially depends on the c-component of the ordered moments; its temperature dependence clearly shows the drastic increase of the c-component in the spiral phase [9]. The temperature dependence of the spectra obtained at the incommensurate zone center, see Fig. 4, show that the two well-separated a-polarized excitations in the spiral phase merge into a broad signal upon heating into the SDW phase. In analogy to the discussion of the low-lying excitations in the spiral phase, one may expect several contributions in the SDW phase as well. Single-ion anisotropy causes a finite energy for the transverse magnetic excitations and will yield a splitting for polarization parallel a and c. Furthermore, there will be a separation due to the phase of the oscillating part which may be either in-phase with the SDW or shifted by $\pi/2$. The in-phase modes are irrelevant for the magnetoelectric coupling at least within the Dzyaloshinski-Moriya scenario of equation (1) since they lead to a collinear spin structure. In contrast, the two $\pi/2$-phase modes may couple with electric polarization even in the paraelectric SDW phase for both magnetic polarizations. Besides the broadening of the neutron signal in the SDW phase, there is a temperature driven change in the spectral weights for the different polarizations. There is still a low-lying $S_\parallel$ contribution in the SDW phase in agreement with the character of the transition into the spiral phase where ordered moments are displaced parallel to the c direction. This low-lying $S_\parallel$ signal can be considered as the quasi-soft mode associated with the SDW to spiral transition. This mode should be strongly coupled to the polarization along c. The total spectral weight of the a- or $S_\perp$-polarized contributions, however, seems not to be focused in a single mode but extends to higher energies. Comparing the response in the $S_\perp$-channel in both phases, one may conclude that the ω_- mode is little changing across the transition, whereas the other $S_\perp$-contribution softens in the SDW phase. These findings agree once more with the IR studies, where the electromagnon for fields along a persists into the paraelectric SDW phase.

In conclusion the INS studies of the magnetic excitations in multiferroic $TbMnO_3$with and without polarization analysis allow us to identify the frequencies and character of the low-energy modes associated with the magnetoelectric coupling. The good agreement of the observed frequencies with those of recent IR studies give strong support to the interpretation as a magnon-phonon hybridized electromagnon mode.

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